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LABORATORY STUDIES OF LOW TEMPERATURE RATE COEFFICIENTS: THE ATMOSPHERIC CHEMISTRY OF THE OUTER PLANETS

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Summary of Research

LABORATORY STUDIES OF LOW TEMPERATURE RATE COEFFICIENTS

During the current NASA grant No. NAGW-2438 (January 1, 1994 - December 31, 1996), laboratory measurements have been carried out to determine low temperature chemical rate coefficients important for the outer planets and their satellites. The effort is directly related to the Cassini mission which will explore Saturn and its satellite Titan. The results provide important laboratory rate coefficient data necessary for modeling planetary atmospheres where accurate rate coefficients at low temperatures are needed.[1] In just the last two years there have been two additional models of Titan,[2,3] as well as a new photochemical model for Jupiter.[4] During the grant period, we have completed the systematic study of the temperature dependence of the kinetic rate coefficients for the ethynyl radical, C_2H with C_2H_2, CH_4, CD_4,[5] C_2H_4, C_2H_6, H_2,[6] C_3H_8, *i*-C_4H_{10}, *n*-C_4H_{10}, *neo*-C_5H_{12}.[7] Preliminary results are also available for reactions of the C_2H radical with several important nitrogen containing species, HCN and CH_3CN.[8] Measurements are carried out using laser photolysis and transient laser absorption techniques and rate coefficients are measured over the temperature range of 150-360 K. These results are summarized in Table I.

Table I. Summary of C_2H reactions studied.

Molecule	Temperature Range (K)	Arrhenius expression (cm^3 $molecules^{-1}$ s^{-1})
C_2H_2	143-359	$^a k_{acetylene} = 8.6\times10^{-16}\ T^{1.8}\exp[(474\pm90)/T]$
CH_4	154-359	$k_{methane} = (1.2\pm0.1)\times10^{-11}\exp[(-491\pm12)/T]$
CD_4	190-359	$k_{d4\text{-}methane} = (8.7\pm1.8)\times10^{-12}\exp[(-650\pm61)/T]$
C_2H_4	150-357	$k_{ethene} = (7.8\pm0.6)\times10^{-11}\exp[(134\pm44)/T]$
C_2H_6	153-357	$k_{ethane} = (3.5\pm0.3)\times10^{-11}\exp[(2.9\pm16)/T]$
H_2	178-359	$k_{hydrogen} = (1.2\pm0.3)\times10^{-11}\exp[(-998\pm57)/T]$
C_3H_8	154-361	$k_{propane} = (7.8\pm0.4)\times10^{-11}\exp[(3\pm12)/T]$
i-C_4H_{10}	177-298	$k_{isobutane} = (8.7\pm0.8)\times10^{-11}\exp[(28\pm21)/T]$
n-C_4H_{10}	176-297	$k_{n\text{-}butane} = (8.3\pm0.6)\times10^{-11}\exp[(112\pm18)/T]$
neo-C_5H_{12}	181-297	$k_{neopentane} = (7.6\pm0.9)\times10^{-11}\exp[(107\pm30)/T]$
HCN	298	$k_{hydrogen\ cyanide} \leq 2\times10^{-12}$
CH_3CN	262-296	$k_{acetonitrile} = 7\times10^{-12}\exp[-507/T]$

[a]Data can be best fit by the corresponding non-Arrhenius expression.

In many cases there are factors of 2 to greater than 10 discrepancies found between the accurately measured values of the low temperature rate coefficients and the values presently incorporated into the models. Below are summaries of our key findings and observations. In Table II, our results for the reactions of C_2H with various hydrocarbons, HCN, and C_2H_2 are compared to values used in the photochemical models of Titan, and Jupiter.

$C_2H + C_2H_2$, C_2H_4

The reaction of C_2H with C_2H_2 is important in the atmosphere of Titan. The previous room temperature rate coefficient data for the $C_2H + C_2H_2$ reaction showed considerable ambiguity. During the current grant period, we have been able to extend our temperature dependence studies down to 143 K. Our experiments not only provide a direct measurement of the rate constant, but also demonstrate the non-Arrhenius behavior of the reaction over the measured temperature range. A test run for the model of Titan was performed by M. Allen (JPL); upon changing the value of the rate coefficient for the $C_2H + C_2H_2$ reaction from 5×10^{-11} to our measured value of 1.5×10^{-10} (actual value) there is an increase in the ethane number density by a factor of ten, and the acetylene number density increases by a factor of two.

The reaction of C_2H with C_2H_4 shows a negative temperature dependence and no pressure dependence. This behavior is attributed to a short-lived addition complex which undergoes unimolecular dissociation to products before it can be stabilized.

$C_2H + H_2$

When there is a predominance of H_2 rather than methane (e.g. Jupiter), C_2H can react with H_2 to form C_2H_2 + H. This reaction has the implication of greatly reducing the abundance of C_2H_6. The $C_2H + H_2$ reaction is also important in that our laboratory results can be directly compared with *ab initio* and transition state calculations which predict non-Arrhenius behavior due to quantum mechanical tunneling and the contribution of the low frequency bending mode vibration to the statistical partitioning in the transition state, respectively.[9,10] When the results of our low temperature work are combined with experimental results over the temperature range 295-854 K, the predicted curvature is observed.[11,12]

$C_2H + CH_4$

The reaction of C_2H with CH_4 is critically important in the balance between CH_4 and C_2H_6. It has been proposed that the photolysis of acetylene by solar radiation, forming C_2H, can catalyze the dissociation of methane to form CH_3 (methyl) radicals; this constitutes a major pathway for the recombination of two methyl radicals to produce ethane. Our measured rated coefficients are much smaller than those previously reported. We have also determined that the reaction of C_2H with CH_4 exhibits a significant kinetic isotope effect ($k_{methane}/k_{d\text{-}4methane}$ = 2.5±0.2 at 300 K).

$C_2H + C_2H_6$, C_3H_8, i-C_4H_{10}, n-C_4H_{10}, neo-C_5H_{12}

Our laboratory measurements for C_2H with C_2H_6, C_3H_8, i-C_4H_{10}, n-C_4H_{10}, neo-C_5H_{12} represent the first low-temperature measurements for any of these processes. The measured rate coefficients differ by up to an order-of-magnitude from those used in the photochemical models. We have also observed that, unlike methane, the temperature dependence can vary from independent of temperature (C_2H_6, C_3H_8) to showing a slight to moderate *negative* temperature dependence. (i-C_4H_{10}, n-C_4H_{10}, neo-C_5H_{12}). This has been interpreted as the possible formation of

collision complexes in the dynamical mechanisms of the reactions. While the mixing ratio for higher molecular weight hydrocarbons is relatively small in the planetary atmospheres, the models become increasingly complex with the introduction of C_3 and higher hydrocarbon photochemistry, including the reactions studied here. The low-temperature rate coefficients will allow for a more refined understanding of the mechanisms of these reactions and their impact on models of the planetary atmospheres.

C_2H + HCN, CH_3CN

Our preliminary measurements for the reaction of C_2H with the nitrogen containing species HCN, CH_3CN are the first direct measurements for these reactions. Since acetylene and polyacetylenes are some of the primary photochemically active species in the atmosphere of Titan, the coupling of the resulting C_2H radicals with the potentially reactive nitrogen compounds is important.

Table II. Comparison of rate constants C_2H + RH, HCN and C_2H_2 with those used in planetary models. k(cm^3 $molecules^{-1}$ s^{-1})

Reaction:	This work[b] (T=140 K)	Yung *et al.*	Toublanc *et al.*	Gladstone *et al.*	Lara *et al.*
$C_2H + CH_4 \rightarrow C_2H_2 + CH_3$	3.6×10^{-13}	4.7×10^{-13}	5.0×10^{-13}	1.5×10^{-12}	4.7×10^{-13}
$C_2H + C_2H_6 \rightarrow C_2H_2 + C_2H_5$	3.6×10^{-11}	6.5×10^{-12}	3.6×10^{-11}	2.1×10^{-11}	2.1×10^{-12}
$C_2H + C_3H_8 \rightarrow C_2H_2 + C_3H_7$	8.0×10^{-11}	1.4×10^{-11}	6.0×10^{-12}	1.4×10^{-11}	1.4×10^{-11}
$C_2H + n\text{-}C_4H_{10} \rightarrow C_2H_2 + C_4H_9$	1.8×10^{-10}	----	----	1.4×10^{-11}	----
$C_2H + i\text{-}C_4H_{10} \rightarrow C_2H_2 + C_4H_9$	1.1×10^{-10}	----	----	1.4×10^{-11}	----
$C_2H + HCN \rightarrow HC_3N + H$	$\leq2\times10^{-12}$	2.2×10^{-12}	2.2×10^{-12}	----	1.1×10^{-11}
$C_2H + C_2H_2 \rightarrow C_4H_2 + H$	1.85×10^{-10}	3.1×10^{-11}	5.6×10^{-11}	1.5×10^{-10}	5×10^{-11}

[b] Calculated from Arrhenius expressions.

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